V.3 Electrocatalytically Active High-Surface-Area Cathodes for Low-Temperature SOFCs

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Objectives

- Develop a fundamental understanding of heterogeneous electrocatalytic phenomena at the surface of ion-conducting ceramics.
- Fabricate high-surface-area solid oxide fuel cell (SOFC) cathodes with controlled microstructure and porosity.
- Develop low-ASR (low area-specific resistance) cathodes for low- to intermediate-temperature SOFCs.

Approach

- Synthesize high-surface-area metal oxide powders and metal oxide powders decorated with nanoclusters of catalytically active metals (Co, Fe, Ni, Ru, and Pt).
- Elucidate the kinetics of surface reactions on these powders via heterogeneous catalysis experiments, such as temperature-programmed desorption (TPD), temperature-programmed reaction (TPR) and isotope exchange.
- Determine the ionic and electronic conductivity of the materials by AC impedance and blocking electrode techniques.
- Determine isothermal stability of the materials.
- Fabricate anode-supported cells using novel processing techniques and evaluate the cathode polarization of the cells.
- Distinguish the individual contributions to electrode polarization by combining the electrochemical characterization with heterogeneous catalysis techniques.

Accomplishments

- Demonstrated stability issues of Ag-ESB (silver – erbia-stabilized bismuth oxide) composite cathodes and improved stability by addition of 10-15 vol% nano-scale yttria-stabilized zirconia (YSZ) powder.
- Synthesized nano-sized $Bi_2Ru_2O_7$, $Pb_2Ru_2O_7$ and doped $Y_2Ru_2O_7$ powders via co-precipitation and a novel wet chemical route.
- Developed higher-conductivity Pr- and Eu-doped $Y_2Ru_2O_7$.
- Developed stable, low-ASR $Bi_2Ru_2O_7$-ESB composite cathodes.

Future Directions

- Improve yield of nano-sized $Bi_2Ru_2O_7$ powders.
- Optimize the microstructure of $Bi_2Ru_2O_7$-ESB composite cathodes.
- Analyze the role of lanthanide dopants and optimize their concentration in the $Bi_2Ru_2O_7$, $Pb_2Ru_2O_7$ and $Y_2Ru_2O_7$ system.

- Characterize catalytic activity by TPD/TPR of ruthenate and Ru-ruthenate system.
- Characterize electrochemical performance by AC impedance and polarization experiments with blocking electrodes.
- Deposit pyrochlore ruthenate cathodes on intermediate-temperature SOFCs and determine their performance.
- Compare catalytic and electrochemical results to elucidate mechanism.

Introduction

For extensive deployment of SOFCs into industrial and consumer markets to become a reality, further performance optimization is necessary. Currently, cathode overpotential is the most significant drag on total SOFC *electrochemical* performance. A significant increase in cathode performance would enable higher power densities at lower temperature and would mean lower cost and therefore greater commercial viability. Towards that end, we are in the process of developing high-performance cathodes for use on conventional (with YSZ electrolyte) and intermediate- to low-temperature (with, e.g., ceria or ceria/bismuth oxide electrolytes) SOFCs.

Approach

The proposed research follows a logical progression: (1) the low-temperature synthesis of high-surface-area metal oxide powders and metal oxide powders decorated with nanoclusters of catalytically active metals (Co, Fe, Ni, Ru, and Pt); (2) the use of heterogeneous catalysis techniques, such as TPD and TPR, and isotope exchange to elucidate the kinetics of surface reactions on these powders; (3) determination of the ionic and electronic conductivity of the materials by AC impedance and blocking electrode analysis; (4) fabrication of anode-supported cells using novel processing techniques; (5) evaluation of the electrode polarization of these cells, combining the electrochemical characterization with heterogeneous catalysis techniques to separate out the individual contributions to the electrode polarization.

Results

Metallic conducting pyrochlores possess a wider conduction band than the semiconducting phases, so the metal-versus-semiconductor dichotomy of the ruthenium pyrochlores is consistent with the Mott–Hubbard mechanism of electron localization. Based on the environment of each O atom shown in Figure 1a, it is expected that the larger the *A* cations, the farther the oxygen atoms will be pushed away from the *A* cations, thereby increasing the Ru–O–Ru angle and shortening the Ru–O bond length. This reasoning predicts a linear relationship between the ionic radii of the *A* cations and the Ru–O–Ru bond angles. This is indeed the case, as shown in Figure 1b, where eight-coordinate ionic radii [1] of the *A* cations (i.e., Bi^{3+}, Pb^{2+}) were used.

Therefore, these ruthenates have the necessary electronic conductivity (~10^3 S/cm), and since the

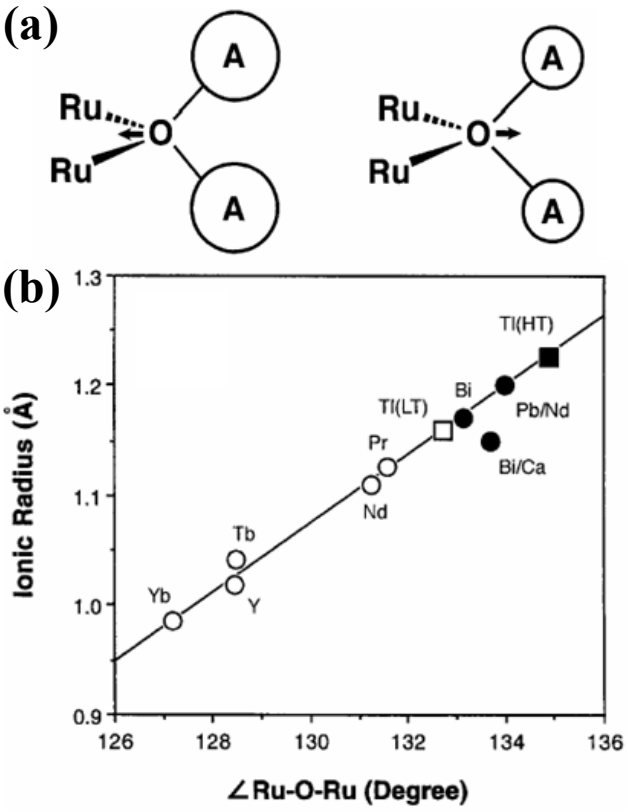

Figure 1. (a) Effect of A Site Cation on Ru-O-Ru Angle; (b) Dependence of Ionic Radius on Ru-O-Ru Angle (adapted from K. S. Lee, *J. Solid State Chem.* 131 (1997), 405)

conduction mechanism is metallic (rather than hopping as in most perovskite materials, e.g., lanthanum strontium manganite), their conductivity increases with decreasing temperature, making them suitable for low- to intermediate-temperature SOFCs. In addition, RuO_2 is known to be catalytically active for oxygen reduction. So a cathode consisting of an ionic phase (e.g., ESB) and an electronic phase (e.g., $Bi_2Ru_2O_7$) and surface decorated with nano particles of RuO_2 should make an ideal cathode. Toward this end, we are investigating $Bi_2Ru_2O_7$, $Pb_2Ru_2O_{6.5}$ and $Y_2Ru_2O_7$.

Bismuth Ruthenate. We obtained phase-pure $Bi_2Ru_2O_7$ after calcination and leaching with HNO_3 to remove the impurity sillenite type-phase. This was annealed with gadolinia-doped ceria (GDC) powder at 850ºC for 10 hours, and x-ray diffraction (XRD) showed there was no reaction between the powders, indicating stability.

An Arrhenius plot of the electrode ASR (cm^2) is shown in Figure 2a with an activation energy of ~1.26 eV. To understand the mechanism of oxygen reduction at the electrodes, impedance measurements were taken as a function of oxygen partial pressure. ASR of the electrode varies with the oxygen partial pressure according to the following equation:

$$[ASR] = [ASR]_o \, (p_{O2})^{-m}$$

The magnitude of the exponent *m* provides insight into the rate-limiting step in the oxygen reduction reaction at the electrodes. Figure 2b is a plot of ln [ASR] vs. ln P_{O2}. The values of *m* range between 0.5 and 0.6, suggesting that the rate-limiting step is surface diffusion of the dissociatively adsorbed oxygen at the electrode surface to the triple phase boundaries (TPBs). Therefore, mixing $Bi_2Ru_2O_7$ with an oxygen ion conducting phase such as ESB should significantly reduce the ASR.

To improve upon the performance of the $Bi_2Ru_2O_7$ cathodes, composite cathodes of $Bi_2Ru_2O_7$ and erbia-stabilized bismuth oxide (BRO-ESB) were fabricated, by solid-state synthesis, and characterized. Figure 3a shows a significant reduction in electrode impedance was achieved by using composite BRO-ESB electrodes, with the lowest impedance (>50% reduction) obtained for a 62.5:37.5 ratio of BRO to ESB. Moreover, switching from single-phase BRO to dual-phase BRO-ESB

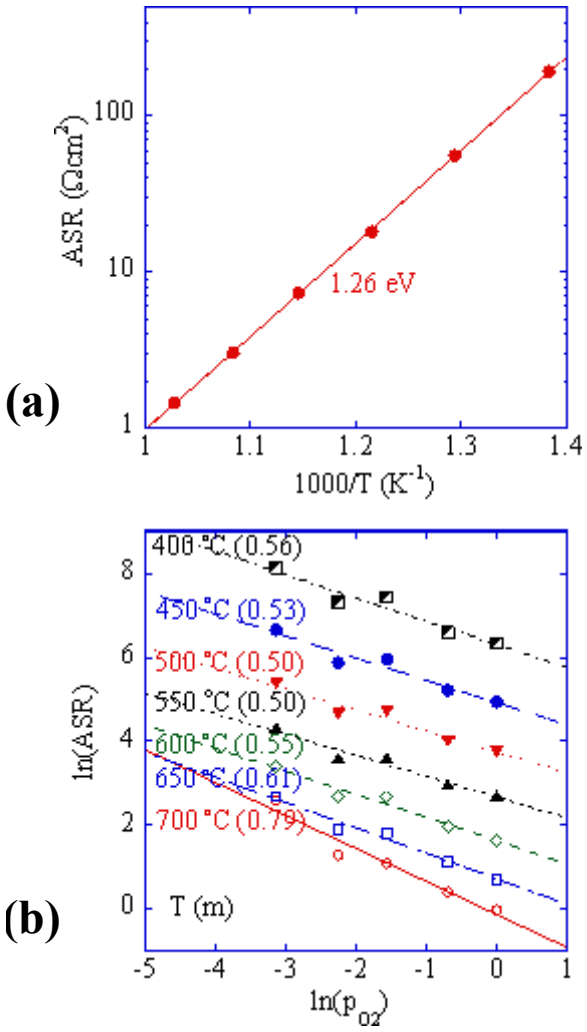

Figure 2. (a) Arrhenius Plot of the $Bi_2Ru_2O_7$ Electrode ASR (cm^2); (b) ln ASR vs. ln P_{O2} at Different Temperatures with *m* in Parenthesis T(*m*)

shifts the rate-limiting step to a much lower frequency (Figure 3b). This may suggest that the rate-limiting step is gas diffusion in the un-optimized BRO-ESB electrode microstructure; hence, even lower electrode impedances may be attainable through tailoring of the electrode microstructure. This will be verified in future experiments. Nevertheless, our initial BRO-ESB electrodes possess among the lowest impedances reported in the literature (Figure 4), with only Ag-ESB composite (which is unstable with time due to Ag migration, described below) and $Ba_xSr_{1-x}Co_yFe_{1-y}O_3$ (one report [2]) reported as better.

Lead Ruthenate. Our studies of $Pb_2Ru_2O_{6.5}$ (PRO) focused on making nano-sized powders for use in composite electrodes. Through novel

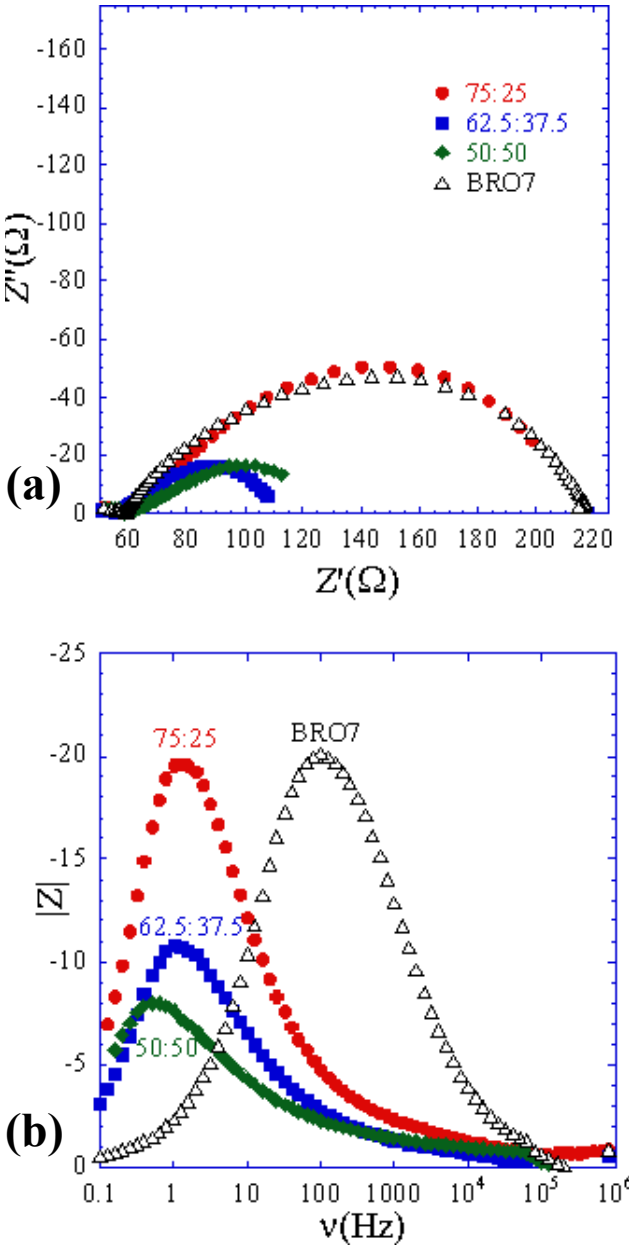

Figure 3. (a) Nyquist and (b) Bode Plots Comparing the Impedance of a $Bi_2Ru_2O_7$ Cathode with Composite $Bi_2Ru_2O_7$-ESB Cathodes in the Ratios 75 (BRO):25 (ESB), 62.5:37.5, 50:50 vol%

processing, we produced PRO crystallites surrounded by even smaller catalytically active RuO_2 particles, thereby obtaining our desired cathode microstructure.

Rare-Earth Doped Yttrium Ruthenate. $Y_2Ru_2O_7$ (YRO) was evaluated as a candidate for an intermediate-temperature SOFC cathode because of its stability in a wide range of temperatures and its lack of reactivity in contact with YSZ and GDC [3]. We prepared nanocrystalline powders of $Y_2Ru_2O_7$ by a co-precipitation method. Phase and morphology were studied by XRD and finite element scanning electron microscopy, showing a particle size of about 100 nm. The nanocrystalline particle size makes the powder amenable for the triple phase boundary tailoring in order to reduce power loss.

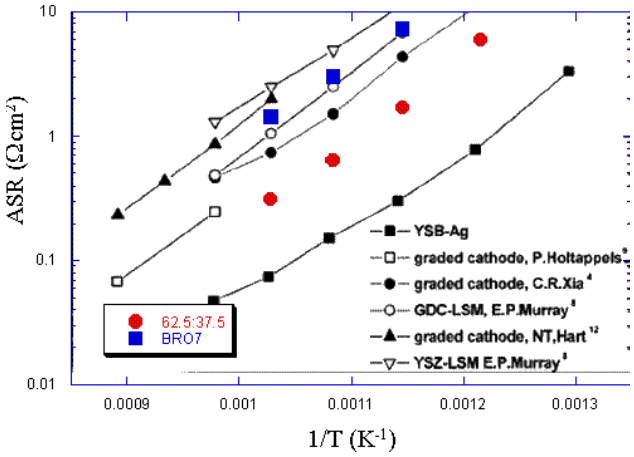

Figure 4. Comparison of ASR of $Bi_2Ru_2O_7$ and $Bi_2Ru_2O_7$-ESB Composite with Recent Literature Results (adapted from C. Xia *et al*, *Appl. Phys. Lett.*, 82 (2003) 10)

In order to obtain a metallic behavior and increase the electrical conductivity of the $Y_2Ru_2O_7$, Eu and Pr were chosen as A-site dopants. XRD confirmed that the doped powders were single-phase, and scanning electron microscopy (SEM)/energy-dispersive x-ray spectroscopy confirmed the presence of the dopant in the pyrochlore structure. The electrical conductivity was measured between 473-1073 K by DC 4-probe method for a dopant range of 5-25 mol%, and our results show that doping increased the conductivity of YRO by 20%.

Ag-ESB Composites. Ag-ESB composites have been described in the literature as possessing one of the lowest ASRs [4]; hence, their long-term stability was examined in order to evaluate the potential of such systems for use as cathodes in intermediate-temperature SOFCs. Cathode ASR was first minimized by optimizing the volume fraction of Ag phase at approximately 50%. The performance of this optimized composition at 600°C is among the

best reported to date. However, the polarization resistance isothermally increases by more than 200% over a seven-day testing period. SEM analysis revealed that the microstructure of the Ag phase undergoes dramatic growth during this timeframe. This microstructural growth and consequent reduction in porosity is believed to diminish cathodic reaction zone size and inhibit gas transport. Nano-scale YSZ ceramic powders were shown to markedly lower the rate of isothermal degradation of these composite cathodes, when added in proper proportion. SEM analysis reveals that the introduction of this third phase helps restrict the mobility of Ag at this temperature, allowing the porosity and reaction zone size to remain relatively high. The optimum YSZ composition appears to be between 10-15 vol%. XRD revealed no evidence of a reaction between the different cathode phases. In SEM micrographs of the microstructure, it was observed that the edges of the Ag particles in the as-fired sample are smooth, while in the tested sample, the edges are rough due to envelopment of YSZ into the Ag particles. It is possible that this effect reduces the triple phase boundaries between the Ag, ESB, and gas phases, contributing to the observed increase in ASR with time for these electrodes.

Conclusions

- Nano-sized $Bi_2Ru_2O_7$, $Pb_2Ru_2O_7$ and doped $Y_2Ru_2O_7$ powders can be synthesized via co-precipitation and a novel wet chemical route.
- $Bi_2Ru_2O_7$-ESB composite cathodes are stable and possess low ASR and impedance.
- $Y_2Ru_2O_7$ conductivity can be increased by 20% by doping with 15 mol% Pr.
- Stability of Ag-ESB composite cathodes can be improved by adding 10-15 vol% nano-scale YSZ powder.

FY 2005 Publications/Presentations

1. "RuO_2 and Pt Based Electrodes for ESB IT-SOFC," V. Esposito, E. Traversa, and E.D. Wachsman, *Solid Oxide Fuel Cells IX*, Electrochem. Soc., S.C. Singhal and J. Mizusaki, Ed.
2. "Bismuth-Ruthenate-Based Cathodes for IT-SOFCs," A. Jaiswal and E.D. Wachsman, *Journal of the Electrochemical Society*, 152, A787-790 (2005).
3. "Preparation and Characterization of Lead Ruthenate Based Composite Cathodes for SOFC Applications," V. Esposito, E. Traversa, and E.D. Wachsman, *Solid State Ionics-2004*, Materials Research Society, P. Knauth, C. Masqulier, E. Traversa, and E.D. Wachsman, Ed., 835, 217-222 (2005).
4. "The Search for a Low Temperature SOFC; How Low Can We Go?" MIT Department of Materials Science Seminar, February 18, 2005, Boston, MA.
5. "Isothermal Stability of Composite Ag-$Er_{0.4}Bi_{1.6}O_3$ Cathodes for Intermediate Temperature Solid Oxide Fuel Cells," American Ceramic Society, 29th International Conference on Advanced Ceramics and Composites, January 24-28, 2005, Cocoa Beach, FL.

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4. C. Xia, Y. Zhang, and M. Liu, *Appl. Phys. Lett*. 82 (2003) 10.